



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 561 600 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
13.09.2000 Bulletin 2000/37

(51) Int. Cl.⁷: **C06B 47/00**

(21) Application number: **93301965.5**

(22) Date of filing: **16.03.1993**

(54) **Water-in-oil emulsions and process for the preparation thereof**

Wasser-in-Öl Emulsionen und Verfahren zur deren Herstellung

Emulsions eau-dans-huile et leur procédé de préparation

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE**

(30) Priority: **17.03.1992 US 852859**

(43) Date of publication of application:
22.09.1993 Bulletin 1993/38

(73) Proprietor:
**THE LUBRIZOL CORPORATION
Wickliffe, Ohio 44092-2298 (US)**

(72) Inventor: **Jahnke, Richard W.
Mentor, Ohio 44060 (US)**

(74) Representative:
**Crisp, David Norman et al
D. YOUNG & CO.
21 New Fetter Lane
London EC4A 1DA (GB)**

(56) References cited:

WO-A-87/03613	WO-A-88/03522
WO-A-89/05848	US-A- 4 234 435
US-A- 5 034 071	US-A- 5 074 939
US-A- 5 076 867	

EP 0 561 600 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] This invention relates to water-in-oil emulsions which are useful as explosives. These emulsions contain at least one emulsifier derived from at least one substituted succinic acylating agent. The substituted succinic acylating agent consists of substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene (e.g., polybutene), said acylating agents being characterized by the presence within their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups.

[0002] Hydrocarbyl-substituted carboxylic acylating agents having at least about 30 aliphatic carbon atoms in the substituent are known. Examples of such acylating agents include the polyisobutenyl-substituted succinic acids and anhydrides. The use of such carboxylic acylating agents as additives in normally liquid fuels and lubricants is disclosed in U.S. Patents 3,288,714 and 3,346,354. These acylating agents are also useful as intermediates for preparing additives for use in normally liquid fuels and lubricants as described in U.S. Patents 2,892,786; 3,087,936; 3,163,603; 3,172,892; 3,189,544; 3,215,707; 3,219,666; 3,231,587; 3,235,503; 3,272,746; 3,306,907; 3,306,908; 3,331,776; 3,341,542; 3,346,354; 3,374,174; 3,379,515; 3,381,022; 3,413,104; 3,450,715; 3,454,607; 3,455,728; 3,476,686; 3,513,095; 3,523,768; 3,630,904; 3,632,511; 3,697,428; 3,755,169; 3,804,763; 3,836,470; 3,862,981; 3,936,480; 3,948,909; 3,950,341; and 4,471,091; and French Patent 2,223,415.

[0003] U.S. Patent 4,234,435 discloses carboxylic acid acylating agents derived from polyalkenes such as polybutenes, and a dibasic carboxylic reactant such as maleic or fumaric acid or certain derivatives thereof. These acylating agents are characterized in that the polyalkenes from which they are derived have an Mn value of about 1300 to about 5000 and an Mw/Mn value of about 1.5 to about 4. The acylating agents are further characterized by the presence within their structure of at least 1.3 groups derived from the dibasic carboxylic reactant for each equivalent weight of the groups derived from the polyalkene. The acylating agents can be reacted with an amine to produce derivatives useful per se as lubricant additives or as intermediates to be subjected to post-treatment with various other chemical compounds and compositions, such as epoxides, to produce still other derivatives useful as lubricant additives.

[0004] Water-in-oil explosive emulsions typically comprise a continuous organic phase (e.g., a carbonaceous fuel) and a discontinuous aqueous phase containing an oxygen-supplying component (e.g., ammonium nitrate). Examples of such water-in-oil explosive emulsions are disclosed in U.S. Patents 3,447,978; 3,765,964; 3,985,593; 4,008,110; 4,097,316; 4,104,092; 4,218,272; 4,259,977; 4,357,184; 4,371,408; 4,391,659; 4,404,050; 4,409,044; 4,448,619; 4,453,989; and 4,534,809; and U.K. Patent Application GB 2,050,340A.

[0005] U.S. Patent 4,216,040 discloses water-in-oil emulsion blasting agents having a discontinuous aqueous phase, a continuous oil or water-immiscible liquid organic phase, and an organic cationic emulsifier having a lipophilic portion and a hydrophilic portion, the lipophilic portion being an unsaturated hydrocarbon chain.

[0006] U.S. Patents 4,708,753 and 4,844,756 disclose water-in-oil emulsions which comprise (A) a continuous oil phase; (B) a discontinuous aqueous phase; (C) a minor emulsifying amount of at least one salt derived from (C)(I) at least one hydrocarbyl-substituted carboxylic acid or anhydride, or ester or amide derivative of said acid or anhydride, the hydrocarbyl substituent of (C)(I) having an average of from about 20 to about 500 carbon atoms, and (C)(II) ammonia or at least one amine; and (D) a functional amount of at least one water-soluble, oil-insoluble functional additive dissolved in said aqueous phase. The '756 patent discloses that component (C)(II) can also be an alkali or alkaline-earth metal. These emulsions are useful as explosive emulsions when the functional additive (D) is an oxygen-supplying component (e.g., ammonium nitrate).

[0007] U.S. Patent 4,710,248 discloses an emulsion explosive composition comprising a discontinuous oxidizer-phase dispersed throughout a continuous fuel phase with a modifier comprising a hydrophilic moiety and a lipophilic moiety. The hydrophilic moiety comprises a carboxylic acid or a group capable of hydrolyzing to a carboxylic acid. The lipophilic moiety is a saturated or unsaturated hydrocarbon chain. The emulsion explosive composition pH is above 4.5.

[0008] U.S. Patent 4,822,433 discloses an explosive emulsion composition comprising a discontinuous phase containing an oxygen-supplying component and an organic medium forming a continuous phase wherein the oxygen-supplying component and organic medium are capable of forming an emulsion which, in the absence of a supplementary adjuvant, exhibits an electrical conductivity measured at 60°C, not exceeding 60,000 picomhos/meter. The reference indicates that the conductivity may be achieved by the inclusion of a modifier which also functions as an emulsifier. The modifier is comprised of a hydrophilic moiety and a lipophilic moiety. The lipophilic moiety can be derived from a poly[alk(en)yl] succinic anhydride. Poly(isobutylene) succinic anhydride having a number average molecular weight in the range of 400 to 5000 is specifically identified as being useful. The hydrophilic moiety is described as being polar in character, having a molecular weight not exceeding 450 and can be derived from polyols, amines, amides, alkanol amines and heterocyclics. Example 14 of this reference discloses the use of a 1:1 condensate of polyisobutenyl succinic anhydride (number average molecular weight = 1200) and dimethylethanol amine as the modifier/emulsifier.

[0009] U.S. Patent 4,828,633 discloses salt compositions which comprise (A) at least one salt moiety derived from (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms, and (A)(II) ammonia, at least

one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; (B) at least one salt moiety derived from (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said acylating agent (B)(I) optionally having at least one hydrocarbyl substituent having an average of up to about 18 carbon atoms, and (B)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; said components (A) and (B) being coupled together by (C) at least one compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group and at least one hydroxyl group. These salt compositions are useful as emulsifiers in water-in-oil explosive emulsions.

10 [0010] U.S. Patents 4,840,687 and 4,956,028 disclose explosive compositions comprising a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one water-immiscible organic liquid, and an emulsifying amount of at least one nitrogen-containing emulsifier derived from (A) at least one carboxylic acylating agent, (B) at least one polyamine, and (C) at least one acid or acid-producing compound capable of forming at least one salt with said polyamine. Examples of (A) include polyisobutenyl succinic acid or anhydride. Examples of (B) include the alkylene polyamines. Examples of (C) include the phosphorus acids (e.g., O,S-dialkylphosphorotriethioic acid). These explosive compositions can be water-in-oil emulsions or melt-in-oil emulsions.

15 [0011] U.S. Patent 4,863,534 discloses an explosive composition comprising a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, and an emulsifying amount of (A) at least one salt composition derived from (A)(1) at least one high-molecular weight hydrocarbyl-substituted carboxylic acid or anhydride, or ester or amide derivative of said acid or anhydride, the hydrocarbyl substituent of (A)(1) having an average of from about 20 to about 500 carbon atoms, and (A)(2) ammonia, at least one amine, at least one alkali or alkaline earth metal compound; and (B) at least one salt composition derived from (B)(1) at least one low-molecular weight hydrocarbyl-substituted carboxylic acid or anhydride, or ester or amide derivative of said acid or anhydride, the hydrocarbyl substituent of (B)(1) having an average of from about 8 to about 18 carbon atoms, and (B)(2) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound.

[0012] U.S. Patent, 4,919,178 discloses emulsifiers which comprise the reaction product of component (I) with component (II). Component (I) comprises the reaction product of certain carboxylic acids or anhydrides, or ester or amide derivatives thereof, with ammonia, at least one amine, at least one alkali and/or at least one alkaline-earth metal. Component (II) comprises certain phosphorous-containing acids; or metal salts of said phosphorous-containing acids, the metals being selected from the group consisting of magnesium, calcium, strontium, chromium, manganese, iron, molybdenum, cobalt, nickel, copper, silver, zinc, cadmium, aluminum, tin, lead, and mixtures of two or more thereof. These emulsifiers are useful in water-in-oil explosive emulsions.

35 [0013] U.S. Patent 4,956,028 discloses an explosive composition which comprises a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one water-immiscible organic liquid, and an emulsifying amount of at least one nitrogen-containing emulsifier derived from (A) at least one carboxylic acylating agent (B) at least one polyamine, and (C) at least one acid or acid-producing compound capable of forming at least one salt with said polyamine. These explosive compositions can be water-in-oil emulsions or melt-in-oil emulsions.

40 [0014] U.S. Patent 4,999,062 describes an emulsion explosive composition comprising a discontinuous phase comprising an oxygen-releasing salt, a continuous water-immiscible organic phase and an emulsifier component comprising a condensation product of a primary amine and a poly[alk(en)yl]succinic acid or anhydride and wherein the condensation product comprises at least 70% by weight succinimide product.

[0015] Water-in-oil explosive emulsions are often blended with ammonium nitrate prills or ANFO for the purpose 45 increasing the explosive energy of such emulsions. Among the commercially available ammonium nitrate prills that are used are those that are made using one or more crystal habit modifiers to control crystal growth and one or more surfactants to reduce caking. A problem with using these treated prills is that they tend to destabilize the emulsions. It would be advantageous to provide explosive emulsions that remain stable when blended with such treated ammonium nitrate prills.

50 [0016] This invention is directed to water-in-oil emulsions which are useful as explosives. These emulsions comprise a discontinuous aqueous phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, and a minor emulsifying amount of at least one emulsifier. The emulsifier is the product made by the reaction of component (A) with component (B): component (A) being at least one substituted succinic acylating agent, said substituted succinic acylating agent consisting of substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene having a number average molecular weight (Mn) of at least 500, said acylating agents being characterized by the presence within their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups; component (B) being ammonia and/or at least one monoamine; and component (A) and component (B) are reacted by means of an acylation reaction and/or under salt-

forming conditions. In one embodiment, these emulsions are stably blended with ammonium nitrate pills that have been made using one or more crystal habit modifiers to control crystal growth and one or more surfactants to reduce caking.

[0017] Various preferred features and embodiments of the invention will be hereinafter described by way of non-limiting illustration.

5 [0018] The term "emulsion" as used in this specification and in the appended claims is intended to cover not only water-in-oil emulsions, but also compositions derived from such emulsions wherein at temperatures below that at which the emulsion is formed the discontinuous phase is solid or in the form of droplets of super-cooled liquid. This term also covers compositions derived from or formulated as such water-in-oil emulsions that are in the form of gelatinous or semi-gelatinous compositions.

10 [0019] The term "hydrocarbyl" is used herein to include:

(1) hydrocarbyl groups, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic groups and the like as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated groups may together form an alicyclic group);

15 (2) substituted hydrocarbyl groups, that is, those groups containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl nature of the hydrocarbyl group; those skilled in the art will be aware of such groups, examples of which include ether, oxo, halo (e.g., chloro and fluoro), alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.;

20 (3) hetero groups, that is, groups which, while having predominantly hydrocarbyl character within the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as pyridyl, furanyl, thiophenyl, imidazolyl, etc.

25 [0020] In general, no more than about three nonhydrocarbon groups or heteroatoms and preferably no more than one, will be present for each ten carbon atoms in a hydrocarbyl group. Typically, there will be no such groups or heteroatoms in a hydrocarbyl group and it will, therefore, be purely hydrocarbyl.

[0021] The hydrocarbyl groups are preferably free from acetylenic unsaturation; ethylenic unsaturation, when present will generally be such that there is no more than one ethylenic linkage present for every ten carbon-to-carbon bonds. The hydrocarbyl groups are often completely saturated and therefore contain no ethylenic unsaturation.

30 [0022] The term "lower" as used herein in conjunction with terms such as alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

[0023] The inventive water-in-oil emulsions, which are useful as explosives, comprise a discontinuous aqueous phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, and a minor emulsifying amount of at least one emulsifier. In one embodiment, these emulsions are stably blended with ammonium nitrate pills that have been treated with surfactants and crystal growth modifiers.

35 [0024] The continuous organic phase is preferably present at a level of at least about 2% by weight, more preferably in the range of about 2% to about 15% by weight, more preferably in the range of about 3.5% to about 10%, more preferably about 5% to about 8% by weight based on the total weight of the water-in-oil emulsion. The discontinuous aqueous phase is preferably present at a level of at least about 85% by weight, more preferably at a level in the range of about 85% to about 98% by weight, more preferably about 92% to about 95% by weight based on the total weight of the emulsion. The emulsifier is preferably present at a level in the range of about 5% to about 95%, more preferably about 5% to about 50%, more preferably about 5% to about 20%, more preferably about 10% to about 20% by weight based on the total weight of the organic phase. The oxygen-supplying component is preferably present at a level in the range of about 70% to about 95% by weight, more preferably about 75% to about 92% by weight, more preferably about 78% to about 90% by weight based on the total weight of the aqueous phase. The water is preferably present at a level in the range of about 5% to about 30% by weight, more preferably about 8% to about 25% by weight, more preferably about 10% to about 22% by weight based on the weight of the aqueous phase.

50 The Carbonaceous Fuel

[0025] The carbonaceous fuel that is useful in the emulsions of the invention can include most hydrocarbons, for example, paraffinic, olefinic, naphthenic, aromatic, saturated or unsaturated hydrocarbons, and is typically in the form of an oil or a wax or a mixture thereof. In general, the carbonaceous fuel is a water-immiscible, emulsifiable hydrocarbon that is either liquid or liquefiable at a temperature of up to about 95°C, and preferably between about 40°C and about 75°C. Oils from a variety of sources, including natural and synthetic oils and mixtures thereof can be used as the carbonaceous fuel.

55 [0026] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-

refined mineral oils of the paraffinic, naphthenic, or mixed paraffin-naphthenic types. Oils derived from coal or shale are also useful. Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkyl benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl) benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); and the like.

[0027] Another suitable class of synthetic oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)-sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like.

[0028] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0029] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of useful oils. These include tetraethyl-silicate, tetraisopropylsilicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methyl-hexyl)-silicate, tetra-(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxo)-di-siloxane, poly(methyl)-siloxanes, poly-(methylphenyl)-siloxanes, etc. Other useful synthetic oils include liquid esters of phosphorus-containing acid (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

[0030] Unrefined, refined and rerefined oils (and mixtures of each with each other) of the type disclosed hereinabove can be used. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except that they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those of skill in the art such as solvent extraction, distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed toward removal of spent additives and oil breakdown products.

[0031] Examples of useful oils include a white mineral oil available from Witco Chemical Company under the trade designation KAYDOL; a white mineral oil available from Shell under the trade designation ONDINA; and a mineral oil available from Pennzoil under the trade designation N-750-HT. Diesel fuel (e.g., Grade No. 2-D as specified in ASTM D-975) can be used as the oil.

[0032] The carbonaceous fuel can be any wax having melting point of at least about 25°C, such as petrolatum wax, microcrystalline wax, and paraffin wax, mineral waxes such as ozocerite and montan wax, animal waxes such as spermacetic wax, and insect waxes such as beeswax and Chinese wax. Useful waxes include waxes identified by the trade designation MOBILWAX 57 which is available from Mobil Oil Corporation; D02764 which is a blended wax available from Astor Chemical Ltd.; and VYBAR which is available from Petrolite Corporation. Preferred waxes are blends of microcrystalline waxes and paraffin.

[0033] In one embodiment, the carbonaceous fuel includes a combination of a wax and an oil. The wax content can be at least about 25% and preferably in the range of about 25% to about 90% by weight of the organic phase, and the oil content can be at least about 10% and preferably ranges from about 10% to about 75% by weight of the organic phase.

The Oxygen-Supplying Component

[0034] The oxygen-supplying component is preferably at least one inorganic oxidizer salt such as ammonium, alkali or alkaline earth metal nitrate, chlorate or perchlorate. Examples include ammonium nitrate, sodium nitrate, calcium nitrate, ammonium chlorate, sodium perchlorate and ammonium perchlorate. Ammonium nitrate is preferred. Mixtures of ammonium nitrate and sodium or calcium nitrate are also useful. In one embodiment, inorganic oxidizer salt comprises principally ammonium nitrate, although up to about 25% by weight of the oxidizer phase can comprise either another inorganic nitrate (e.g., alkali or alkaline earth metal nitrate) or an inorganic perchlorate (e.g., ammonium perchlorate or an alkali or alkaline earth metal perchlorate) or a mixture thereof.

The Emulsifier

[0035] The terms "substituent" and "acylating agent" or "substituted succinic acylating agent" are to be given their normal meanings. For example, a substituent is an atom or group of atoms that has replaced another atom or group in a molecule as a result of a reaction. The term acylating agent or substituted succinic acylating agent refers to the compound per se and does not include unreacted reactants used to form the acylating agent or substituted succinic acylating agent.

[0036] The substituted succinic acylating agent (A) utilized in the preparation of the emulsifier can be characterized by the presence within its structure of two groups or moieties. The first group or moiety is referred to hereinafter, for convenience, as the "substituent group(s)" and is derived from a polyalkene. The polyalkene from which the substituted groups are derived is characterized by an Mn (number average molecular weight) value of at least about 500, more preferably at least about 1000, more preferably at least about 1300, more preferably at least about 1500. Advantageously, the polyalkene has an Mn in the range of about 500 to about 10,000, more preferably about 1000 to about 7000, more preferably about 1300 to about 5000, more preferably about 1500 to about 5000, more preferably about 1500 to about 3000, more preferably about 1500 to about 2400, more preferably about 1500 to about 2000, more preferably about 1600 to about 1900. The polyalkene preferably has an Mw/Mn value of at least about 1.5, preferably from about 1.5 to about 5, more preferably about 2 to about 5, more preferably about 2.8 to about 5, more preferably about 2.8 to about 4.5, more preferably about 3.3 to about 3.9. The abbreviation Mw is the conventional symbol representing the weight average molecular weight.

[0037] Gel permeation chromatography (GPC) is a method which provides both weight average and number average molecular weights as well as the entire molecular weight distribution of the polymers. For purpose of this invention a series of fractionated polymers of isobutene, polyisobutene, is used as the calibration standard in the GPC. The techniques for determining Mn and Mw values of polymers are well known and are described in numerous books and articles. For example, methods for the determination of Mn and molecular weight distribution of polymers is described in W.W. Yau, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatographs", J.Wiley & Sons, Inc., 1979.

[0038] Polyalkenes having the Mn and Mw values discussed above are known in the art and can be prepared according to conventional procedures. For example, some of these polyalkenes are described and exemplified in U.S. Patent 4,234,435. The disclosure of this patent relative to such polyalkenes is hereby incorporated by reference. Several such polyalkenes, especially polybutenes, are commercially available.

[0039] The second group or moiety in the acylating agent is referred to herein as the "succinic group(s)". The succinic groups are those groups characterized by the structure



wherein X and X' are the same or different provided that at least one of X and X' is such that the substituted succinic acylating agent can function as a carboxylic acylating agent. That is, at least one of X and X' must be such that the substituted acylating agent can form, for example, amides, imides or amine salts with amino compounds, and esters, ester-salts, amides, imides, etc., with the hydroxyamines, and otherwise function as a conventional carboxylic acid acylating agent. Transesterification and transamidation reactions are considered, for purposes of this invention, as conventional acylating reactions.

[0040] Thus, X and/or X' is usually -OH, -O-hydrocarbyl, -O-M⁺ where M⁺ represents one equivalent of a metal, ammonium or amine cation, -NH₂, -Cl, -Br, and together, X and X' can be -O- so as to form the anhydride. The specific identity of any X or X' group which is not one of the above is not critical so long as its presence does not prevent the remaining group from entering into acylation reactions. Preferably, however, X and X' are each such that both carboxyl functions of the succinic group (i.e., both -C(O)X and -C(O)X') can enter into acylation reactions.

[0041] One of the unsatisfied valences in the grouping



of Formula I forms a carbon-to-carbon bond with a carbon atom in the substituent group. While other such unsatisfied valence may be satisfied by a similar bond with the same or different substituent group, all but the said one such valence

[0043] The ratio of succinic groups to equivalents of substituent groups present in the acylating agent can be determined by one skilled in the art using conventional techniques (e.g., acid number, saponification number).

[0044] In one embodiment, the succinic groups correspond to the formula



wherein R and R' are each independently selected from the group consisting of -OH, -Cl, -O-lower alkyl, and when taken together, R and R' are -O-. In the latter case, the succinic group is a succinic anhydride group. All the succinic groups in a particular succinic acylating agent need not be the same, but they can be the same. Preferably, the succinic groups correspond to



and mixtures of III(a) and III(b). Providing substituted succinic acylating agents wherein the succinic groups are the same or different is within the ordinary skill of the art and can be accomplished through conventional procedures such as treating the substituted succinic acylating agents themselves (for example, hydrolyzing the anhydride to the free acid or converting the free acid to an acid chloride with thionyl chloride) and/or selecting the appropriate maleic or fumaric reactants.

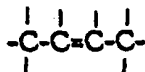
[0045] The preferred characteristics of the succinic acylating agents are intended to be understood as being both independent and dependent. They are intended to be independent in the sense that, for example, a preference for a minimum of 1.4 or 1.5 succinic groups per equivalent weight of substituent groups is not tied to a more preferred value of Mn or Mw/Mn. They are intended to be dependent in the sense that, for example, when a preference for a minimum of 1.4 or 1.5 succinic groups is combined with more preferred values of Mn and/or Mw/Mn, the combination of preferences does in fact describe still further more preferred embodiments of the invention. Thus, the various parameters are intended to stand alone with respect to the particular parameter being discussed but can also be combined with other parameters to identify further preferences. This same concept is intended to apply throughout the specification with respect to the description of preferred values, ranges, ratios, reactants, and the like unless a contrary intent is clearly demonstrated or apparent.

[0046] The polyalkenes from which the substituent groups are derived are homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms; usually 2 to about 6 carbon atoms. The interpolymers

are those in which two or more olefin monomers are interpolymerized according to well-known conventional procedures to form polyalkenes having units within their structure derived from each of said two or more olefin monomers. Thus, "interpolymer(s)" as used herein is inclusive of copolymers, terpolymers, tetrapolymers, and the like. As will be apparent to those of ordinary skill in the art, the polyalkenes from which the substituent groups are derived are often conventionally referred to as "polyolefin(s)".

[0047] The olefin monomers from which the polyalkenes are derived are polymerizable olefin monomers characterized by the presence of one or more ethylenically unsaturated groups (i.e., $>C=C<$); that is, they are monoolefinic monomers such as ethylene, propylene, butene-1, isobutene, and octene-1 or polyolefinic monomers (usually diolefinic monomers) such as butadiene-1,3 and isoprene.

[0048] These olefin monomers are usually polymerizable terminal olefins; that is, olefins characterized by the presence in their structure of the group $>C=CH_2$. However, polymerizable internal olefin monomers (sometimes referred to in the literature as medial olefins) characterized by the presence within their structure of the group



can also be used to form the polyalkenes. When internal olefin monomers are employed, they normally will be employed with terminal olefins to produce polyalkenes which are interpolymers. For purposes of this invention, when a particular polymerized olefin monomer can be classified as both a terminal olefin and an internal olefin, it will be deemed to be a terminal olefin. Thus, pentadiene-1,3 (i.e., piperylene) is deemed to be a terminal olefin for purposes of this invention.

[0049] Some of the substituted succinic acylating agents (A) useful in preparing the inventive emulsifiers are known in the art and are described in, for example, U.S. Patent 4,234,435, the disclosure of which is hereby incorporated by reference. The acylating agents described in the '435 patent are characterized as containing substituent groups derived from polyalkenes having an Mn value of about 1300 to about 5000, and an Mw/Mn value of about 1.5 to about 4.

[0050] There is a general preference for aliphatic, hydrocarbon polyalkenes free from aromatic and cycloaliphatic groups. Within this general preference, there is a further preference for polyalkenes which are derived from the group consisting of homopolymers and interpolymers of terminal hydrocarbon olefins of 2 to about 16 carbon atoms. This further preference is qualified by the proviso that, while interpolymers of terminal olefins are usually preferred, interpolymers optionally containing up to about 40% of polymer units derived from internal olefins of up to about 16 carbon atoms are also within a preferred group. A more preferred class of polyalkenes are those selected from the group consisting of homopolymers and interpolymers of terminal olefins of 2 to about 6 carbon atoms, more preferably 2 to 4 carbon atoms. However, another preferred class of polyalkenes are the latter more preferred polyalkenes optionally containing up to about 25% of polymer units derived from internal olefins of up to about 6 carbon atoms. The polybutenes and polyisobutenes are particularly preferred. In one embodiment, the polyalkene is a polybutene in which at least about 50% of the total units derived from butenes is derived from isobutene. In one embodiment, the polyalkene is an interpolymer or copolymer of ethylene and propylene, or an interpolymer or copolymer of styrene and at least one diene (e.g., butadiene, pentadiene, isoprene, etc.).

[0051] The preparation of polyalkenes as described above which meet the various criteria for Mn and Mw/Mn is within the skill of the art and does not comprise part of the present invention. Techniques readily apparent to those skilled in the art include controlling polymerization temperatures, regulating the amount and type of polymerization initiator and/or catalyst, employing chain terminating groups in the polymerization procedure, and the like. Other conventional techniques such as stripping (including vacuum stripping) a very light end and/or oxidatively or mechanically degrading high molecular weight polyalkene to produce lower molecular weight polyalkenes can also be used.

[0052] In preparing the substituted succinic acylating agents of this invention, one or more of the above-described polyalkenes is reacted with one or more acidic reactants selected from the group consisting of maleic or fumaric reactants of the general formula



wherein X and X' are as defined hereinbefore in Formula I. Preferably the maleic and fumaric reactants will be one or more compounds corresponding to the formula



wherein R and R' are as previously defined in Formula II herein. Ordinarily, the maleic or fumaric reactants will be maleic acid, fumaric acid, maleic anhydride, or a mixture of two or more of these. The maleic reactants are usually preferred over the fumaric reactants because the former are more readily available and are, in general, more readily

reacted with the polyalkenes (or derivatives thereof) to prepare the substituted succinic acylating agents of the present invention. The especially preferred reactants are maleic acid, maleic anhydride, and mixtures of these. Due to availability and ease of reaction, maleic anhydride will usually be employed.

[0053] For convenience and brevity, the term "maleic reactant" is sometimes used to refer to the acidic reactants used to prepare the succinic acylating agents. When used, it should be understood that the term is generic to acidic reactants selected from maleic and fumaric reactants corresponding to Formulae (IV) and (V) above including mixtures of such reactants.

[0054] Examples of patents describing various procedures for preparing useful acylating agents include U.S. Patents 3,215,707; 3,219,666; 3,231,587; 3,912,764; 4,110,349; 4,234,435; and 5,041,662; and U.K. Patents 1,440,219 and 1,492,337. The disclosures of these patents are hereby incorporated by reference for their teachings with respect to the preparation of substituted succinic acylating agents.

[0055] The acylating agents described above are intermediates in the process for preparing the emulsifier for the inventive emulsion, the process comprising reacting (A) one or more acylating agents with (B) ammonia and/or at least one monoamine.

[0056] The amines (B) useful in making the emulsifiers include primary amines, secondary amines and tertiary amines, with the secondary and tertiary amines being preferred and the tertiary amines being particularly useful. Hydroxy amines, especially tertiary alkanol monoamines, are also useful. Mixtures of two or more amines can be used.

[0057] The amines can be aliphatic, cycloaliphatic, aromatic or heterocyclic, including aliphatic-substituted aromatic, aliphatic-substituted cycloaliphatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic, heterocyclic-substituted aliphatic, heterocyclic-substituted cycloaliphatic and heterocyclic-substituted aromatic amines. These amines may be saturated or unsaturated. If unsaturated, the amine is preferably free from acetylenic unsaturation. The amines may also contain non-hydrocarbon substituents or groups as long as these groups do not significantly interfere with the reaction of the amines with the acylating agents (A). Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl, mercapto, nitro, and interrupting groups such as -O- and -S- (e.g., as in such groups as -CH₂CH₂-X-CH₂CH₂- where X is -O- or -S-).

[0058] With the exception of the high molecular weight hydrocarbyl-substituted amines described more fully hereinafter, the amines used in this invention ordinarily contain less than about 40 carbon atoms in total and usually not more than about 20 carbon atoms in total.

[0059] Aliphatic monoamines include mono-aliphatic, di-aliphatic and tri-aliphatic-substituted amines wherein the aliphatic groups can be saturated or unsaturated and straight or branched chain. Such amines include, for example, mono-, di- and tri-alkyl-substituted amines; mono-, di- and tri-alkenyl-substituted amines; amines having one or more N-alkenyl substituents and one or more N-alkyl substituents, and the like. The total number of carbon atoms in these aliphatic monoamines preferably does not exceed about 40 and usually does not exceed about 20 carbon atoms. Specific examples of such monoamines include ethylamine, di-ethylamine, tri-ethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl laurylamine, oleylamine, N-methyl-octylamine, dodecylamine, octadecylamine, and the like. Examples of cycloaliphatic-substituted aliphatic amines, aromatic-substituted aliphatic amines, and heterocyclic-substituted aliphatic amines, include 2-(cyclohexyl)-ethylamine, benzylamine, phenylethylamine, and 3-(furylpropyl) amine.

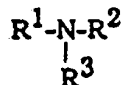
[0060] Cycloaliphatic monoamines are those monoamines wherein there is one cycloaliphatic substituent attached directly to the amino nitrogen through a carbon atom in the cyclic ring structure. Examples of cycloaliphatic monoamines include cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines, N-ethyl-cyclohexylamines, dicyclohexylamines, and the like. Examples of aliphatic-substituted, aromatic-substituted, and heterocyclic-substituted cycloaliphatic monoamines include propyl-substituted cyclohexylamines, phenyl-substituted cyclopentylamines and pyranil-substituted cyclohexylamine.

[0061] Suitable aromatic amines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthylene. Examples of aromatic monoamines include aniline, di(para-methylphenyl) amine, naphthylamine, N-(n-butyl) aniline, and the like. Examples of aliphatic-substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines include para-ethoxyaniline, paradodecylamine, cyclohexyl-substituted naphthylamine and thienyl-substituted aniline.

[0062] Heterocyclic amines can also be used. As used herein, the terminology "heterocyclic amine(s)" is intended to describe those heterocyclic amines containing a primary, secondary or tertiary amino group and at least one nitrogen as a heteroatom in the heterocyclic ring. Heterocyclic amines can be saturated or unsaturated and can contain various substituents such as nitro, alkoxy, alkyl mercapto, alkyl, alkenyl, aryl, alkaryl, or aralkyl substituents. Generally, the total number of carbon atoms in the substituents will not exceed about 20. Heterocyclic amines can contain heteroatoms other than nitrogen, especially oxygen and sulfur. Obviously they can contain more than one nitrogen heteroatom. The 5- and 6-membered heterocyclic rings are preferred.

[0063] Among the suitable heterocyclics are aziridines, azetidines, azolidines, tetra- and di-hydro pyridines, pyrroles, indoles, piperadines, imidazoles, di- and tetra-hydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkyl-morpholines, N-aminoalkylthiomorpholines, N-aminoalkyl-piperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydroderivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl-substituted piperidines, piperazine, aminoalkyl-substituted piperazines, morpholine, aminoalkyl-substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are useful. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, and N-aminoethylpiperazine.

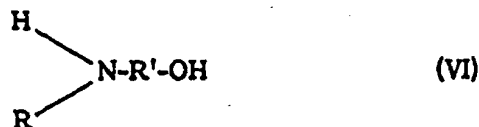
[0064] The tertiary amines can be represented by the formula.



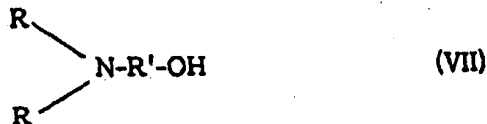
wherein R^1 , R^2 and R^3 are the same or different hydrocarbyl groups. Preferably, R^1 , R^2 and R^3 are independently hydrocarbyl groups of from 1 to about 20 carbon atoms. Examples of useful tertiary amines include trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, monomethyldiethyl amine, monoethyldimethyl amine, dimethylpropyl amine, dimethylbutyl amine, dimethylpentyl amine, dimethylhexyl amine, dimethylheptyl amine, dimethyloctyl amine, dimethylnonyl amine, dimethyldodecyl amine, dimethyldicodanyl amine, dimethylphenyl amine, N,N-dioctyl-1-octanamine, N,N-didodecyl-1-dodecanamine, N,N-dimethyl-1-tetradecanamine, N,N-dimethyl-1-hexadecanamine, N,N-dimethyl-1-octadecanamine, N,N-dimethylcoco amine, N,N-dimethyl soyaamine, N,N-dimethyl hydrogenated tallow amine, etc.

[0065] Hydroxyamines analogous to those amines described herein are also useful. The hydroxy-substituted amines contemplated are those having hydroxy substituents bonded directly to a carbon atom other than a carbonyl carbon atom; that is, they have hydroxy groups capable of functioning as alcohols. The hydroxyamines can be primary, secondary or tertiary amines, with the secondary and tertiary amines being preferred, and the tertiary amines being especially preferred. The terms "hydroxyamine" and "aminoalcohol" describe the same class of compounds and, therefore, can be used interchangeably.

[0066] The hydroxyamines include N-(hydroxyl-substituted hydrocarbyl) amines, hydroxyl-substituted poly(hydrocarbyloxy) analogs thereof and mixtures thereof. These include secondary and tertiary alkanol amines represented, respectfully, by the formulae:



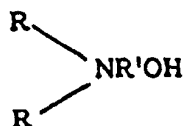
and



wherein each R is independently a hydrocarbonyl group of one to about eight carbon atoms or hydroxyl-substituted hydrocarbonyl group of two to about eight carbon atoms and R' is a divalent hydrocarbonyl group of about two to about 18 carbon atoms. The group -R'-OH in such formulae represents the hydroxyl-substituted hydrocarbonyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylenes, 1,2-octadecylene, etc. group. Where two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R is a lower alkyl group of up to seven carbon atoms.

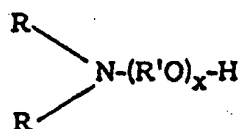
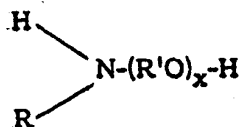
[0067] Examples of the N-(hydroxyl-substituted hydrocarbonyl) amines include di- and triethanolamine, dimethylethanolamine, diethylethanolamine, di-(3-hydroxypropyl) amine, N-(3-hydroxybutyl) amine, N-(4-hydroxybutyl) amine, N,N-di-(2-hydroxypropyl) amine, N-(2-hydroxyethyl) morpholine and its thio analog, N-(2-hydroxyethyl) cyclohexylamines, N-3-hydroxyl cyclopentylamine, o-, m- and p-aminophenol, N-(hydroxyethyl) piperazine, N,N-di(hydroxyethyl) piperazine, and the like.

[0068] In a particularly advantageous embodiment, the hydroxyamine is a compound represented by the formula



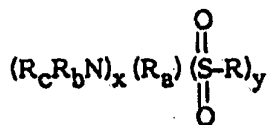
wherein each R is independently an alkyl group of 1 to about 4 carbon atoms, preferably 1 or 2 carbon atoms, and R' is an alkylene group of 2 to about 4 carbon atoms, preferably about 2 or 3 carbon atoms. In an especially useful embodiment, the hydroxyamine is dimethylethanolamine.

[0069] The hydroxyamines can also be either N-(hydroxy-substituted hydrocarbonyl)amines. These are hydroxyl-substituted poly(hydrocarbonyloxy) analogs of the above-described hydroxy amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbonyl) amines can be conveniently prepared by reaction of epoxides with afore-described amines and can be represented by the formulae:



wherein x is a number of about 2 to about 15, and R and R' are as described above with respect to Formulae (VI) and (VII).

[0070] Also suitable as amines are the aminosulfonic acids and derivatives thereof corresponding to the formula:



5

wherein R is OH, NH₂, ONH₄, etc.; R_a is a polyvalent organic group having a valence equal to x + y; R_b and R_c are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl with the proviso that at least one of R_b and R_c is hydrogen per aminosulfonic acid molecule; x is one and y is an integer equal to or greater than one. Each aminosulfonic reactant is characterized by one HN< or H₂N- group and at least one

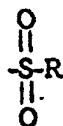
15



20

group. These sulfonic acids can be aliphatic, cycloaliphatic or aromatic aminosulfonic acids and the corresponding functional derivatives of the sulfo group. Specifically, the aminosulfonic acids can be aromatic aminosulfonic acids, that is, where R_a is a polyvalent aromatic group such as phenylene where at least one

25



30

group is attached directly to a nuclear carbon atom of the aromatic group. The aminosulfonic acid is a mono-amino aliphatic sulfonic acid; that is, an acid where x is one and R_a is a polyvalent aliphatic group such as ethylene, propylene, trimethylene, and 2-methylene propylene. Other suitable aminosulfonic acids and derivatives thereof useful as amines in this invention are disclosed in U.S. Patents 3,029,250; 3,367,864; and 3,926,820; which are incorporated herein by reference.

35

[0071] The high molecular weight hydrocarbyl amines which can be used as amines in this invention are generally prepared by reacting a chlorinated polyolefin having a molecular weight of at least about 400 with ammonia or an amine. The amines that can be used are known in the art and described, for example, in U.S. Patents 3,275,554 and 3,438,757, both of which are incorporated herein by reference. These amines must possess a primary or secondary amino group.

40

[0072] The carboxylic derivative compositions produced from the acylating agents (A) and ammonia or the amines (B) described hereinbefore comprise acylated amines which typically include one or more amine salts, amides, imides and/or imidazolines as well as mixtures of two or more thereof. When the amine (B) is a hydroxyamine, the carboxylic derivative compositions usually include esters and/or ester-salts (e.g., half-ester and half-salt). The amine salt can be an external salt wherein the ionic salt linkage is formed between the acylating agent (A) and a nitrogen atom from the amine (B); the amine is not otherwise bonded to the acylating agent. The amine salt can also be an internal salt wherein the acylating agent (A) and amine (B) are bonded to each other through a non-salt linkage (e.g., an ester linkage) and a nitrogen atom from the bonded amine forms a salt linkage with the acylating agent. Examples of these salts are as follows:

50

55



1.5



25

30

35

40

45

50

55

[0078] An equivalent weight of a hydroxyamine to be reacted with the acylating agent under amide- or imide-forming conditions is its molecular weight. Under such conditions, the hydroxyl groups are ignored when calculating equivalent weight. Thus, ethanolamine would have an equivalent weight equal to its molecular weight, and diethanolamine would have an equivalent weight (based on nitrogen) equal to its molecular weight when such amines are reacted under amide- or imide-forming conditions.

[0079] The
tions is its mol
ignored. Thus,
its molecular we

5 [0080] The
of th carboxylic
A-C. In the follo
grade, and all p

10 Example 1

[0081] A mi
to 138°C. This m
reaction mixture
15 a polyisobutene-
dride content of
flash point of 180
to equivalent we

20 Example 2

[0082] A mix
to 110°C. This m
surface. At 190-1
25 heating at 190-19
acylating agent h

Example 3

30 [0083] A mixt
dride is heated to
beneath the surfa
stripped by heatin
tuted succinic acy
35 94.

Example 4

[0084] A mixtu
40 of polyisobutene (P
0.5 hour. The reac
filtrate is the desir
94 as determined b

45 Example 5

[0085] A mixtur
to 140°C. This mixt
the surface. The rea
50 at 203°C. The reac
agent having a sap

Example 6

55 [0086] A mixtur
at 220°C for 8 hours
beneath the surface
stripped under vacu

stituted succinic acylating agent.

Example 7

- 5 [0087] A mixture of 800 parts of a polyisobutene falling within the scope of the claims of the present invention and having an Mn of about 2000, 646 parts of mineral oil and 87 parts of maleic anhydride is heated to 179°C in 2.3 hours. At 176-180°C, 100 parts of gaseous chlorine is added beneath the surface over a 19 hour period. The reaction mixture is stripped by blowing with nitrogen for 0.5 hour at 180°C. The residue is an oil-containing solution of the desired polyisobutene-substituted succinic acylating agent.

Example 8

- 10 [0088] The procedure for Example 2 is repeated except the polyisobutene (Mn=1845; Mw=5325) is replaced on an equimolar basis by polyisobutene (Mn=1457; Mw=5808).

Example 9

- 15 [0089] The procedure for Example 2 is repeated except the polyisobutene (Mn=1845; Mw=5325) is replaced on an equimolar basis by polyisobutene (Mn=2510; Mw=5793).

Example 10

- 20 [0090] The procedure for Example 2 is repeated except the polyisobutene (Mn=1845; Mw=5325) is replaced on an equimolar basis by polyisobutene (Mn=3220; Mw=5660).

Example A

- 25 [0091] A mixture of 4920 parts (8.32 equivalents) of the polyisobutene-substituted succinic acylating agent prepared in accordance with the teachings of Example 1 and 2752 parts of a 40 Neutral oil are heated to 50-55°C with stirring. 742 parts (8.32 equivalents) of dimethylethanolamine are added over a period of 6 minutes. The reaction mixture exotherms to 59°C. The reaction mixture is heated to 115°C over a period of 3 hours. Nitrogen blowing is commenced at a rate of 1.5 standard cubic feet per hour, and the reaction mixture is heated to 135°C over a period of 0.5 hour. The mixture is heated to and maintained at a temperature of 140-160°C for 14 hours, then cooled to room temperature to provide the desired product. The product has a nitrogen content of 1.35% by weight, a total acid number of 13.4, a total base number of 54.8, a viscosity at 100°C of 125 cSt, a viscosity at 40°C of 2945 cSt, a specific gravity at 15.6°C of 0.94, and a flash point of 82°C.

Example B

- 40 [0092] A mixture of 1773 parts (3 equivalents) of the polyisobutene-substituted succinic acylating agent prepared in accordance with the teachings of Example 1 and 992 parts of a 40 Neutral oil are heated to 80°C with stirring. 267 parts (3 equivalents) of dimethylethanolamine are added over a period of 6 minutes. The reaction mixture is heated to 132°C over a period of 2.75 hours. The mixture is heated to and maintained at a temperature of 150-174°C for 12 hours, then cooled to room temperature to provide the desired product. The product has a nitrogen content of 0.73% by weight, a total acid number of 12.3, a total base number of 29.4, a viscosity at 100°C of 135 cSt, a viscosity at 40°C of 2835 cSt, a specific gravity at 15.6°C of 0.933, and a flash point of 97°C.

Example C

- 50 [0093] The procedure of Example B is repeated except that after the product is cooled to room temperature, 106 parts of dimethylethanolamine are added with stirring. The resulting product has a nitrogen content of 1.21% by weight, a total acid number of 11.3, a total base number of 48.9, a viscosity at 100°C of 110 cSt, a viscosity at 40°C of 2730 cSt, a specific gravity at 15.6°C of 0.933, and a flash point of 90°C.

55 Sensitizers

- [0094] In one embodiment of the invention, closed-cell, void-containing materials are used as sensitizing components. The term "closed-cell, void-containing material" is used herein to mean any particulate material which comprises

closed cell, hollow cavities. Each particle of the material can contain one or more closed cells, and the cells can contain a gas, such as air, or can be evacuated or partially evacuated. In one embodiment of the invention, sufficient closed cell, void containing material is used to yield a density in the resulting emulsion of from about 0.8 to about 1.35 g/cc, more preferably about 0.9 to about 1.3 g/cc, more preferably about 1.1 to about 1.3 g/cc. In general, the emulsions of the subject invention can contain up to about 15% by weight, preferably from about 0.25% to about 15% by weight of the sub-cell void containing material. Preferred closed cell void containing materials are discrete glass spheres having a particle size within the range of about 10 to about 175 microns. In general, the bulk density of such particles can be within the range of about 0.1 to about 0.4 g/cc. Useful glass microbubbles or microballoons which can be used are the microbubbles sold by 3M Company and which have a particle size distribution in the range of from about 10 to about 160 microns and a nominal size in the range of about 60 to 70 microns, and densities in the range of from about 0.1 to about 0.4 g/cc. Microballoons identified by the industry designation C15/250 which have a particle density of 0.15 gm/cc and 10% of such microballoons crush at a static pressure of 250 psig can be used. Also, microballoons identified by the designation B37/2000 which have a particle density of 0.37 gm/cc and 10% of such microballoons crush at a static pressure of 2000 psig can be used. Other useful glass microballoons are sold under the trade designation of ECCOSPHERES by Emerson & Cumming, Inc., and generally have a particle size range from about 44 to about 175 microns and a bulk density of about 0.15 to about 0.4 g/cc. Other suitable microballoons include the inorganic microspheres sold under the trade designation of Q-CEL by Philadelphia Quartz Company.

[0095] The closed cell, void containing material can be made of inert or reducing materials. For example, phenol-formaldehyde microbubbles can be utilized within the scope of this invention. If the phenol-formaldehyde microbubbles are utilized, the microbubbles themselves are a fuel component for the explosive and their fuel value should be taken into consideration when designing a water-in-oil emulsion explosive composition. Another closed cell, void containing material which can be used within the scope of the subject invention is the saran microspheres sold by Dow Chemical Company. The saran microspheres have a diameter of about 30 microns and a particle density of about 0.032 g/cc. Because of the low bulk density of the saran microspheres, it is preferred that only from about 0.25 to about 1% by weight thereof be used in the water-in-oil emulsions of the subject invention.

[0096] Gas bubbles which are generated in-situ by adding to the composition and distributing therein a gas-generating material such as, for example, an aqueous solution of sodium nitrite, can also be used to sensitize the explosive emulsions. Other suitable sensitizing components which may be employed alone or in addition to the foregoing include insoluble particulate solid self-explosives or fuel such as, for example, grained or flaked TNT, DNT, RDX and the like, aluminum, aluminum alloys, silicon and ferrosilicon; and water-soluble and/or hydrocarbon-soluble organic sensitizers such as, for example, amine nitrates, alkanolamine nitrates, hydroxyalkyl nitrates, and the like. The explosive emulsions of the present invention may be formulated for a wide range of applications. Any combination of sensitizing components may be selected in order to provide an explosive composition of virtually any desired density, weight-strength or critical diameter. The quantity of solid self-explosives or fuels and of water-soluble and/or hydrocarbon-soluble organic sensitizers may comprise up to about 50% by weight of the total explosive composition. The volume of the occluded gas component may comprise up to about 50% of the volume of the total explosive composition.

Particulate-Solid Oxygen-Supplying Salts

[0097] In one embodiment, particulate-solid oxygen-supplying salts may be incorporated into or blended with the inventive emulsions to increase the explosive energy of such emulsions. These salts can be ammonium nitrate, sodium nitrate, calcium nitrate or mixtures of two or more thereof. Ammonium nitrate is particularly useful. These particulate solids can be in the form of prills, crystals or flakes. Ammonium nitrate prills are especially useful.

[0098] In one embodiment ammonium nitrate prills made by the Kaltenbach-Thoring (KT) process are used. This process involves the use of one or more crystal growth modifiers to help control the growth of the crystals. It also involves the use of one or more surfactants which are used to reduce caking. An example of a commercially available material made by this process is Columbia KT ammonium nitrate prills which are marketed by Columbia Nitrogen. The crystal habit modifier and the surfactant used in the production of Columbia KT prills are each available under the trade designation Galoryl.

[0099] Ammonium nitrate particulate solids, (e.g., ammonium nitrate prills), which are available in the form of pre-blended ammonium nitrate-fuel oil (ANFO) mixtures, can be used. Typically, ANFO contains about 94% by weight ammonium nitrate and about 6% fuel oil (e.g., diesel fuel oil), although these proportions can be varied.

[0100] The quantities of these particulate-solid oxygen-supplying salts or ANFO that are used can comprise up to about 80% by weight of the total explosive composition. In one embodiment of the invention, explosive compositions comprising about 25% to about 35% by weight of the inventive emulsion and about 65% to about 75% of particulate solid, oxygen-supplying salts or ANFO are used. In one embodiment, explosive compositions comprising about 45% to about 55% by weight of the inventive emulsion and about 45% to about 55% of particulate solid, oxygen-supplying salts or ANFO are used. In one embodiment, explosive compositions comprising about 70% to about 80% by weight of the

inventive emulsion and about 20% to about 30% of particulate solid, oxygen-supplying salts or ANFO are used.

Supplemental Additives

5 [0101] Supplemental additives may be incorporated in the emulsions of the invention in order to further improve sensitivity, density, strength, rheology and cost of the final explosive. Typical of materials found useful as optional additives include, for example, particulate non-metal fuels such as sulfur, gilsonite and the like; particulate inert materials such as sodium chloride, barium sulphate and the like; thickeners such as guar gum, polyacrylamide, carboxymethyl or ethyl cellulose, biopolymers, starches, elastomeric materials, and the like; crosslinkers for the thickeners such as potassium pyroantimonate and the like; buffers or pH controllers such as sodium borate, zinc nitrate and the like; crystals habit modifiers such as alkyl naphthalene sodium sulphonate and the like; liquid phase extenders such as formamide, ethylene glycol and the like; and bulking agents and additives of common use in the explosives art. The quantities of supplemental additives used may comprise up to about 50% by weight of the total explosive composition.

15 Method of Making the Emulsions

[0102] A useful method for making the emulsions of the invention comprises the steps of (1) mixing water, inorganic oxidizer salts (e.g., ammonium nitrate) and, in certain cases, some of the supplemental water-soluble compounds, in a first premix, (2) mixing the carbonaceous fuel, the emulsifier of the invention and any other optional oil-soluble compounds, in a second premix and (3) adding the first premix to the second premix in a suitable mixing apparatus, to form a water-in-oil emulsion. The first premix is heated until all the salts are completely dissolved and the solution may be filtered if needed in order to remove any insoluble residue. The second premix is also heated to liquefy the ingredients. Any type of apparatus capable of either low or high shear mixing can be used to prepare these water-in-oil emulsions. Closed-cell, void containing materials, gas-generating materials, solid self-explosive ingredients such as particulate TNT, particulate-solid oxygen-supplying salts such as ammonium nitrate prills and ANFO, solid fuels such as aluminum or sulfur, inert materials such as barytes or sodium chloride, undissolved solid oxidizer salts and other optional materials, if employed, are added to the emulsion and simply blended until homogeneously dispersed throughout the composition.

[0103] The water-in-oil explosive emulsions of the invention can also be prepared by adding the second premix liquefied organic solution phase to the first premix hot aqueous solution phase with sufficient stirring to invert the phases. However, this method usually requires substantially more energy to obtain the desired dispersion than does the preferred reverse procedure. Alternatively, these water-in-oil explosive emulsions are particularly adaptable to preparation by a continuous mixing process where the two separately prepared liquid phases are pumped through a mixing device wherein they are combined and emulsified.

35 [0104] The emulsifiers of this invention can be added directly to the inventive emulsions. They can also be diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain from about 10% to about 90% by weight of the emulsifier composition of this invention and may contain, in addition, one or more other additives known in the art or described hereinabove.

40 [0105] Examples I-IX are directed to explosive emulsions using the emulsifier prepared in accordance with the teachings of Example A. The formulations for these explosive emulsions are indicated below in Table I (all numerical amounts being in grains). The procedure for making these emulsions involves the following steps. The ammonium nitrate is mixed with the water at a temperature of 82°C. The emulsifier is mixed with the mineral oil at a temperature of 52°C. The mixture of ammonium nitrate and water is added to the mixture of oil and emulsifier to form a water-in-oil emulsion. The glass microballoons are then added. Each of these explosive emulsions are useful as blasting agent.

TABLE I

Example No.	I	II	III	IV	V	VI	VII	VIII	IX
50 Ammonium Nitrate	7440	7636	7636	7200	8500	7700	7200	8500	7700
Water	1610	1564	1564	2000	1000	1500	2000	1000	1500
Klearol oil (refined mineral oil, Witco)	800	---	---	---	---	---	---	---	---
55 Mentor 28 (mineral seal oil, Exxon)	---	700	---	---	---	---	---	---	---
40 Neutral Oil	---	---	700	700	400	750	100	100	50
C15/250 Glass Microballoons	100	100	100	100	250	150	100	250	150

TABLE I (continued)

Example No.	I	II	III	IV	V	VI	VII	VIII	IX
Product of Ex. A	150	100	100	100	100	50	700	400	750

Example X

[0106] The following emulsion is prepared using Columbia KT ammonium nitrate prills (a product of Columbia Nitrogen identified as ammonium nitrate prills made using the Kaltenbach-Thoring process employing a crystal growth modifier and a surfactant, each of which is available under the trade designation Galoryl). The formulation for this emulsion is provided in Table II (all numerical amounts being in grams).

TABLE II

Ammonium Nitrate	534.52
Columbia KT prills	229.08
Water	156.40
40 Neutral oil	65.00
Product of Ex. A	15.00

[0107] The emulsion in Table II is prepared by mixing the ammonium nitrate with the water and then melting the Columbia KT prills in the ammonium nitrate and water. The emulsifier from Example A is mixed with the 40 Neutral oil. The mixture of ammonium nitrate, water and Columbia KT prills is added to the mixture of oil and emulsifier. The resulting emulsion is creamy (no graininess) three months after it is made.

[0108] Examples XI-XIX are directed to explosive compositions consisting of mixtures of the emulsions from Examples I-III and ANFO. The ANFO is a mixture of ammonium nitrate solids (94% by weight) and diesel fuel oil (6% by weight). The formulations are indicated in Table III (all numerical amounts being in grams).

TABLE III

Example No.	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
Emulsion from Ex. I	300	---	---	500	---	---	750	---	---
Emulsion from Ex. II	---	300	---	---	500	---	---	750	---
Emulsion from Ex. III	---	---	300	---	---	500	---	---	750
ANFO	700	700	700	500	500	500	250	250	250

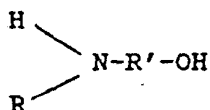
Claims

1. A water-in-oil emulsion useful as an explosive comprising: a discontinuous aqueous phase comprising at least one oxygen-supplying component; a continuous organic phase comprising at least one carbonaceous fuel; and a minor emulsifying amount of at least one emulsifier made by the reaction of component (A) with component (B),

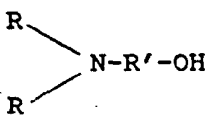
component (A) being at least one substituted succinic acylating agent, said substituted succinic acylating agent consisting of substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene having a number average molecular weight (Mn) of at least 500, said acylating agents having within their structure an average of at least 1.3 succinic groups for each equivalent weight of substituent groups, component (B) being ammonia and/or at least one monoamine, and component (A) and component (B) are reacted by means of an acylation reaction and/or under salt-forming conditions.

2. The emulsion of claim 1 wherein said acylating agents have within their structure about 1.5 to about 2.5 succinic groups for each equivalent weight of substituent groups.

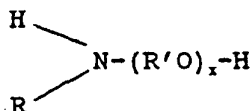
3. The emulsion of claim 1 or claim 2 wherein the value of Mw/Mn for said polyalkene is from about 1.5 to about 5.
4. The emulsion of claim 1 or 2 wherein said polyalkene has an Mn value of about 1300 to about 5000 and an Mw/Mn value of about 2.8 to about 5.
5. The emulsion of any preceding claim wherein the substituent groups in component (A) are derived from one or more polyalkenes selected from homopolymers and interpolymers of terminal olefins of from 2 to about 16 carbon atoms with the proviso that said interpolymers can optionally contain up to about 25% of polymer units derived from internal olefins of up to about 6 carbon atoms.
6. The emulsion of any preceding claim wherein the substituent groups in component (A) are derived from a polybutene, ethylene-propylene interpolymer, styrene-diene interpolymer, or a mixture of two or more of any of these.
7. The emulsion of any preceding claim wherein the substituent groups in component (A) are derived from polybutene in which at least about 50% of the total units derived from butenes is derived from isobutene.
8. The emulsion of any preceding claim wherein component (B) is selected from: at least one monoamine, at least one hydroxyamine, at least one tertiary amine, at least one alkanol tertiary monoamine, secondary alkanol amines represented by the formula



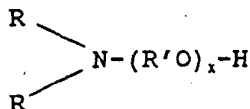
tertiary alkanol amines represented by the formula



hydroxyl-substituted oxyalkylene secondary alkanol amines represented by the formula



hydroxyl-substituted oxyalkylene tertiary alkanol amines represented by the formula



wherein x is from about 2 to about 15, each R is independently a hydrocarbyl group of 1 to about 8 carbon atoms or a hydroxyl-substituted hydrocarbyl group of 2 to about 8 carbon atoms and R' is a divalent hydrocarbyl group of 2 to about 18 carbon atoms, and mixtures of two or more of the amines.

9. The emulsion of any one of claims 1 - 7 wherein component (B) is dimethyl ethanolamine.
10. The emulsion of any preceding claim wherein the ratio of equivalents of component (A) to component (B) is in the range of about 1:0.5 to about 1:3.

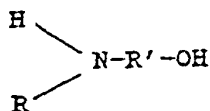
11. The emulsion of any preceding claim wherein said oxygen supplying component is ammonium nitrate and/or one or more alkali or alkaline earth metal nitrates, chlorates or perchlorates.
12. The emulsion of any preceding claim wherein said carbonaceous fuel is a water-immiscible, emulsifiable hydrocarbon that is either liquid or liquefiable at a temperature up to about 95°C.
13. The emulsion of any preceding claim wherein said discontinuous aqueous phase is present at a level of about 85% to about 98% by weight based on the weight of said emulsion and said continuous organic phase is present at a level of about 2% to about 15% by weight based on the weight of said emulsion, said oxygen-supplying component is present at a level in the range of about 70% to about 95% by weight based on the weight of said aqueous phase, and said emulsifier is present at a level in the range of about 5% to about 95% by weight based upon the weight of said organic phase.
14. The emulsion of any preceding claim wherein said emulsion contains a sensitizing amount of at least one closed-cell, void-containing material or a sensitizing amount of gas bubbles.
15. The emulsion of any preceding claim wherein said emulsion contains up to about 80% by weight of particulate solid oxygen-containing salts dispersed therein.
16. The emulsion of claim 15 wherein said particulate solids are selected from ammonium nitrate, sodium nitrate, calcium nitrate and mixtures of two or more thereof.
17. The emulsion of any preceding claim wherein component (B) is dimethylethanolamine and said emulsion contains up to about 80% by weight of ammonium nitrate particulate solids, said ammonium nitrate particulate solids being made using at least one crystal habit modifier and at least one surfactant.
18. The emulsion of any preceding claim wherein said emulsion contains up to about 80% by weight of a preblended ammonium nitrate-fuel oil mixture.
19. The emulsion of any preceding claim wherein said emulsion contains up to about 50% by weight of a particulate metal fuel selected from aluminum, aluminum alloys, silicon and ferro-silicon.
20. The emulsion of any preceding claim wherein said emulsion contains a thickening amount of at least one thickener.
21. A process for the preparation of a water-in-oil emulsion of claim 1 which comprises admixing an aqueous phase comprising at least one oxygen-supplying component and an organic phase comprising at least of carbonaceous fuel in the presence of a minor emulsifying amount of at least one emulsifier as defined in claim 1.

Patentansprüche

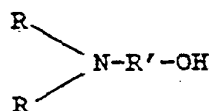
1. Wasser-in-Öl-Emulsion, die als Sprengstoff geeignet ist, umfassend:
 - eine diskontinuierliche wäßrige Phase umfassend mindestens eine Sauerstoffliefernde Komponente;
 - eine kontinuierliche organische Phase umfassend mindestens einen kohlenstoffhaltigen Brennstoff;
 - eine geringe emulgierende Menge mindestens eines Emulgators, der durch Umsetzung der Komponente (A) mit Komponente (B) hergestellt wird, wobei
 - Komponente (A) mindestens ein substituiertes Bernsteinsäureacylierungsmittel ist, das aus Substituentengruppen und Bernsteinsäuregruppen besteht, wobei die Substituentengruppen von einem Polyalken mit einem Zahlenmittel des Molekulargewichts (Mn) von mindestens 500 abgeleitet sind, wobei die Acylierungsmittel in ihrer Struktur mindestens 1,3 Bernsteinsäuregruppen pro Äquivalentgewicht der Substituentengruppen enthalten,
 - Komponente (B) Ammoniak und/oder mindestens ein Monoamin ist, und
 - Komponente (A) und Komponente (B) mittels einer Acylierungsreaktion und/oder unter salzbildenden Bedin-

gungen umgesetzt werden.

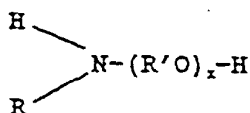
2. Emulsion nach Anspruch 1, wobei die Acylierungsmittel in ihrer Struktur etwa 1,5 bis etwa 2,5 Bernsteinsäuregruppen pro Äquivalentgewicht der Substituentengruppen enthalten.
3. Emulsion nach Anspruch 1 oder 2, wobei der Mw/Mn-Wert des Polyalkens etwa 1,5 bis etwa 5 beträgt.
4. Emulsion nach Anspruch 1 oder 2, wobei das Polyalken einen Mn-Wert von etwa 1300 bis etwa 5000 und einen Mw/Mn-Wert von etwa 2,8 bis etwa 5 aufweist.
5. Emulsion nach einem der vorstehenden Ansprüche, wobei die Substituentengruppen in Komponente (A) von einem oder mehr Polyalken(en) ausgewählt aus Homopolymeren und Copolymeren von endständigen Olefinen mit 2 bis etwa 16 Kohlenstoffatomen abgeleitet sind, mit der Maßgabe, dass die Copolymere gegebenenfalls bis zu etwa 25% Polymereinheiten enthalten können, die von internen Olefinen mit bis zu etwa 6 Kohlenstoffatomen abgeleitet sind.
6. Emulsion nach einem der vorstehenden Ansprüche, wobei die Substituentengruppen in Komponente (A) von einem Polybuten, Ethylen-Propylen-Copolymer, Styrol-Dien-Copolymer, oder einem Gemisch von zwei oder mehr davon abgeleitet sind.
7. Emulsion nach einem der vorstehenden Ansprüche, wobei die Substituentengruppen in Komponente (A) von Polybuten abgeleitet sind, worin mindestens etwa 50 % der gesamten von Butenen abgeleiteten Einheiten von Isobuten abgeleitet sind.
8. Emulsion nach einem der vorstehenden Ansprüche, wobei Komponente (B) ausgewählt ist aus: mindestens einem Monoamin, mindestens einem Hydroxyamin, mindestens einem tertiären Amin, mindestens einem tertiären Alkanol-Monoamin, sekundären Alkanolaminen der allgemeinen Formel



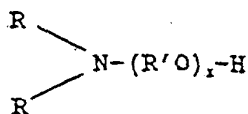
tertiären Alkanolaminen der allgemeinen Formel



Hydroxyl-substituierten sekundären Oxyalkylen-Alkanolaminen der allgemeinen Formel



Hydroxyl-substituierten tertiären Oxyalkylen-Alkanolaminen der allgemeinen Formel



wobei x einen Wert von etwa 2 bis etwa 15 hat, jeder Rest R unabhängig eine Hydrocarbylgruppe mit 1 bis etwa 8 Kohlenstoffatomen oder eine Hydroxyl-substituierte Hydrocarbylgruppe mit 2 bis etwa 8 Kohlenstoffatomen und R' eine divalente Hydrocarbylgruppe mit 2 bis etwa 18 Kohlenstoffatomen ist, und Gemischen von zwei oder mehr dieser Amine.

9. Emulsion nach einem der Ansprüche 1 bis 7, wobei Komponente (B) Dimethylethanolamin ist.
10. Emulsion nach einem der vorstehenden Ansprüche, wobei das Verhältnis der Äquivalente der Komponente (A) zu Komponente (B) im Bereich von etwa 1:0,5 bis etwa 1:3 liegt.
11. Emulsion nach einem der vorstehenden Ansprüche, wobei die Sauerstoff-liefernde Komponente Ammoniumnitrat und/oder ein oder mehr Alkali- oder Erdalkalimetallnitrat(e), -chlorat(e) oder -perchlorat(e) ist.
12. Emulsion nach einem der vorstehenden Ansprüche, wobei der kohlenstoffhaltige Brennstoff ein mit Wasser nicht mischbarer, emulgierbarer Kohlenwasserstoff ist, der bei einer Temperatur von bis zu etwa 95°C entweder flüssig oder verflüssigbar ist.
13. Emulsion nach einem der vorstehenden Ansprüche, wobei die diskontinuierliche wäßrige Phase in einer Menge von etwa 85 Gew.-% bis etwa 98 Gew.-% auf der Basis des Emulsionsgewichts, die kontinuierliche organische Phase in einer Menge von etwa 2 Gew.-% bis etwa 15 Gew.-% auf der Basis des Emulsionsgewichts, die Sauerstoff-liefernde Komponente in einer Menge im Bereich von etwa 70 Gew.-% bis etwa 95 Gew.-% auf der Basis des Gewichts der wäßrigen Phase und der Emulgator in einer Menge im Bereich von etwa 5 Gew.-% bis etwa 95 Gew.-% auf der Basis des Gewichts der organischen Phase vorliegt.
14. Emulsion nach einem der vorstehenden Ansprüche, wobei die Emulsion eine sensibilisierende Menge mindestens eines geschlossenzelligen Hohlräume-enthaltenden Materials oder eine sensibilisierende Menge von Gasblasen enthält.
15. Emulsion nach einem der vorstehenden Ansprüche, wobei in der Emulsion bis zu etwa 80 Gew.-% teilchenförmige, feste Sauerstoff-enthaltende Salze dispergiert sind.
16. Emulsion nach Anspruch 15, wobei die teilchenförmigen Feststoffe aus Ammoniumnitrat, Natriumnitrat, Calciumnitrat und Gemischen von zwei oder mehr davon ausgewählt sind.
17. Emulsion nach einem der vorstehenden Ansprüche, wobei Komponente (B) Dimethylethanolamin ist und die Emulsion bis zu etwa 80 Gew.-% teilchenförmiges festes Ammoniumnitrat enthält, wobei das teilchenförmige feste Ammoniumnitrat unter Verwendung mindestens eines Kristalltracht-Modifikationsmittels und mindestens eines Tensids hergestellt worden ist.
18. Emulsion nach einem der vorstehenden Ansprüche, wobei die Emulsion bis zu etwa 80 Gew.-% eines vorgemischten Ammoniumnitrat-Brennöl-Gemisches enthält.
19. Emulsion nach einem der vorstehenden Ansprüche, wobei die Emulsion bis zu etwa 50 Gew.-% eines teilchenförmigen Metall-Brennstoffs ausgewählt aus Aluminium, Aluminiumlegierungen, Silicium und Ferrosilicium enthält.
20. Emulsion nach einem der vorstehenden Ansprüche, wobei die Emulsion eine verdickende Menge mindestens eines Verdickungsmittels enthält.
21. Verfahren zur Herstellung einer Wasser-in-Öl-Emulsion gemäß Anspruch 1, umfassend Mischen einer wäßrigen Phase umfassend mindestens eine Sauerstoff-liefernde Komponente mit einer organischen Phase umfassend

mindestens einen kohlenstoffhaltigen Brennstoff in Gegenwart einer geringen emulgierenden Menge mindestens eines Emulgators gemäß Anspruch 1.

Revendications

5

1. Emulsion eau-dans-huile utile en tant qu'explosif comprenant: une phase aqueuse discontinue comprenant au moins un composant fournissant de l'oxygène; une phase organique continue comprenant au moins un combustible carboné; et une petite quantité d'émulsifiant d'au moins un émulsifiant fabriquée par la réaction du composant (A) avec le composant (B),

10

le composant (A) étant au moins un agent acylant succinique substitué, ledit agent acylant succinique substitué se composant de groupes substituants et de groupes succiniques dans lesquels les groupes substituants sont dérivés d'un polycalcène ayant une masse moléculaire moyenne en nombre (Mn) d'au moins 500, lesdits agents acylants ayant dans leur structure une moyenne d'au moins 1,3 groupe succinique pour chaque poids équivalent de groupes substituants;

15

le composant (B) étant l'ammoniac et/ou au moins une monoamine; et

le composant (A) et le composant (B) sont mis à réagir à l'aide d'une réaction d'acylation et/ou dans des conditions de formation de sel.

20

2. Emulsion selon la revendication 1, dans laquelle lesdits agents acylants ont dans leur structure d'environ 1,5 à environ 2,5 groupes succiniques pour chaque poids équivalent de groupes substituants.

3. Emulsion selon la revendication 1 ou 2, dans laquelle la valeur de Mm/Mn pour ledit polycalcène est d'environ 1,5 à environ 5.

25

4. Emulsion selon la revendication 1 ou 2, dans laquelle ledit polycalcène possède une valeur Mn d'environ 1 300 à environ 5 000 et une valeur Mm/Mn d'environ 2,8 à environ 5.

30

5. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle les groupes substituants dans le composant (A) sont dérivés d'un ou plusieurs polycalcènes choisis parmi les homopolymères et interpolymères d'oléfines terminales de 2 à environ 16 atomes de carbone à condition que lesdits interpolymères puissent éventuellement contenir jusqu'à environ 25% de motifs polymères dérivés d'oléfines internes jusqu'à environ 6 atomes de carbone.

35

6. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle les groupes substituants dans le composant (A) sont dérivés d'un polybutène, d'un interpolymère éthylène/propylène, d'un interpolymère styrène-diène ou d'un mélange de deux ou plusieurs de ceux-ci.

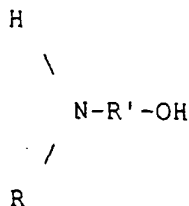
40

7. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle les groupes substituants dans le composant (A) sont dérivés du polybutène dans lequel au moins environ 50% des motifs totaux dérivés de butènes sont dérivés de l'isobutène.

45

8. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le composant (B) est choisi parmi: au moins une monoamine, au moins une hydroxylamine, au moins une amine tertiaire, au moins une alcanolmonoamine tertiaire, les alcanolamines secondaires représentées par la formule:

50



55

les alcanolamines tertiaires représentées par la formule:



les alcanol(oxyalkylène)amines secondaires à substitution hydroxyle représentées par la formule:



25 les alcanol(oxyalkylène)amines tertiaires à substitution hydroxyle représentées par la formule:



40 dans laquelle x vaut d'environ 2 à environ 15, chaque R est indépendamment un groupe hydrocarbyle de 1 à environ 8 atomes de carbone ou un groupe hydrocarbyle à substitution hydroxyle de 2 à environ 8 atomes de carbone et R' est un groupe hydrocarbyle divalent de 2 à environ 18 atomes de carbone, et les mélanges de deux ou plusieurs des amines.

- 45 9. Emulsion selon l'une quelconque des revendications 1 à 7, dans laquelle le composant (B) est la diméthyléthanolamine.
10. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le rapport d'équivalents du composant (A) au composant (B) est dans la gamme d'environ 1:0,5 à environ 1:3.
- 50 11. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle ledit composant fournissant de l'oxygène est le nitrate d'ammonium et/ou un ou plusieurs nitrates, chlorates ou perchlorates de métal alcalin ou alcalino-terreux.
- 55 12. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le combustible carboné est un hydrocarbure émulsifiable, immiscible dans l'eau qui est soit liquide, soit liquéfiable à une température jusqu'à environ 95°C.
13. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle la phase aqueuse discontinue est

présente à une teneur d'environ 85% à environ 98% en poids par rapport au poids de ladite émulsion et ladite phase organique continue st présente à une teneur d'environ 2% à environ 15% en poids par rapport au poids de ladite émulsion, ledit composant fournissant de l'oxygène est présent à une teneur dans la gamine d'environ 70% à environ 95% en poids par rapport au poids de ladite phase aqueuse, et ledit émulsifiant est présent à une teneur dans la gamme d'environ 5% à environ 95% en poids par rapport au poids de ladite phase organique.

14. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle ladite émulsion contient une quantité sensibilisante d'au moins une matière contenant des vides, à cellules fermées ou une quantité de bulles de gaz.
15. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle ladite émulsion contient dispersés à l'intérieur jusqu'à 80% en poids de sels solides et particuliers contenant de l'oxygène.
16. Emulsion selon la revendication 15, dans laquelle lesdits solides particuliers sont choisis parmi le nitrate d'ammonium, le nitrate de sodium, le nitrate de calcium et leurs mélanges de deux ou plus.
17. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le composant (B) est la diméthyléthanolamine et ladite émulsion contient jusqu'à environ 80% en poids de solides particuliers de nitrate d'ammonium, lesdits solides particuliers de nitrate d'ammonium étant fabriqués en utilisant un modificateur de la forme caractéristique de cristal et au moins un tensio-actif.
18. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle ladite émulsion contient jusqu'à environ 80% en poids d'un mélange prémélangé de nitrate d'ammonium/fioul.
19. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle ladite émulsion contient jusqu'à environ 50% en poids d'un combustible métallique particulière choisi parmi l'aluminium, les alliages d'aluminium, le silicium et le ferro-silicium.
20. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle ladite émulsion contient une quantité épaississante d'au moins un épaississant.
21. Procédé pour la préparation d'une émulsion eau-dans-huile selon la revendication 1, qui consiste à mélanger une phase aqueuse comprenant au moins un composant fournissant de l'oxygène et une phase organique comprenant au moins un combustible carboné en présence d'une petite quantité émulsifiante d'au moins un émulsifiant tel que défini selon la revendication 1.

